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RAPID METHOD OF CALCULATING THE HIGH-TEMPERATURE HEAT CAPACITY OF SOLID INORGANIC COMPOUNDS

D.Sh.Tsagareyshvili and G.G.Gvelesiani*

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Description of a rapid method of determining the coefficients a, b, and c in the Maier-Kelley empirical equation $C^{aT} = a + bT - cT^{-2}$, for the atomic heat capacity of a substance. Empirical equations for the three coefficients are set up, based on the temperature dependence of corundum. Theoretical and experimental high-temperature heat-capacity values for various inorganic and some organic solid compounds are tabulated.

Author

For many inorganic solid compounds there are no mathematical equations of high-temperature heat capacity based on experimental data (Bibl.1, 2). A number of approximate methods of calculating the heat capacities of solid bodies at elevated temperatures are known (Bibl.2 - 6).

In this paper, a rapid method is proposed for determining the coefficients a, b, and c in the empirical Maier-Kelley equation (Bibl.7) for the dependence of the heat capacity of a substance at constant pressure, $C_p^{a\,t}$, on the absolute temperature T:

$$C_p^{aT} = a + bT - cT^{-2}.$$

(1)

An equation of dependence of the atomic heat capacity of a substance at constant volume, $C_v^{a\,t}$, on the quantity $\frac{\Theta}{T}$ has been derived in simplified form

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** Numbers in the margin indicate pagination in the original foreign text.

where the coefficients a_0 and b_0 are, respectively, equal to $0.87 \cdot K$ and $6.6 \cdot K$. To establish their values, we used the equation of the temperature dependence of C_p^{at} of α-corundum, Al_2O_3, as being the most reliable. In addition, the temperature slope of its heat capacity in the $298 - 2000^{\circ}K$ interval is satisfactorily expressed ($\pm 0.5\%$) by eq.(1). Thus, the values of the coefficients $a = 5.50$ and $b = 0.564 \times 10^{-3}$ for the atomic heat capacity of corundum (Bibl.1) are entirely reliable. The Debye characteristic temperature Θ, in calculating C_p by the present method, is computed from the value of the standard atomic entropy S_{298}^{at} by the formula (Bibl.8):

$$\Theta = 1130 \left[\exp\left(\frac{S_{298}^{aT}}{3} \right) - 0.78 \right]^{-1/3}. \tag{5}$$

The value of Θ calculated from eq.(5) for corundum was $931^{\circ}K$. Consequently,

$$a_0 = (5.96 - a) \frac{T_{mp}}{C_{p298}^{aT} \cdot \Theta} = (5.96 - 5.5) \frac{2305}{3.78 \times 931} = 0.3;$$

$$b_0 = \frac{T_{mp} \cdot b}{C_{p298}^{aT}} = \frac{2305 \cdot 0.564 \cdot 10^{-3}}{3.78} = 0.34.$$

Thus, the coefficients a and b of eq.(1) should be determined from the following relations:

$$a = 5.96 - \frac{0.3 \times C_{p298}^{aT} \cdot \Theta}{T_{mp}}, \tag{6}$$

$$b = \frac{0.34 \times C_{p298}^{aT}}{T_{mp}}. \tag{7}$$

The coefficient c is calculated from the value of C_{p298}^{at} from eq.(1):

$$c = 0.9 \, (a + b \cdot 298 - C_{p298}^{aT}) \cdot 10^5. \tag{8}$$

If the resultant values of the coefficients a_0 and b_0 for corundum are <u>/583</u> constant for various types of compounds, the method may be recommended for use. It was, therefore, necessary to check the accuracy of the computational formu-

3

for the Debye function (Bibl.8):

$$C_v^{aT} = \frac{120}{18.5 + \left(\dfrac{\Theta}{T}\right)^2} - 0.5 , \tag{2}$$

where Θ is the characteristic temperature in $^\circ K$. Equation (2) may take the form

$$C_v^{aT} = 5.96 - \frac{(C_v^{aT} + 0.5)\,\Theta^2}{18.5} T^{-2}.$$

In order to pass from $C_v^{a\,t}$ to $C_p^{a\,t}$, we make use of the Nernst-Lindemann semi-empirical relation (Bibl.9)

$$C_p^{aT} = C_v^{aT} + 0.0214\,(C_p^{aT})^2\,\frac{T}{T_{mp}} ,$$

where T_{mp} is the melting point of the compound, in $^\circ K$. Consequently,

$$C_p^{aT} = 5.96 + \frac{0.0214\,(C_p^{aT})^2}{T_{mp}}\,T - \frac{(C_v^{aT} + 0.5)\,\Theta^2}{18.5}\,T^{-2}. \tag{3}$$

Equation (3), containing terms in T and T^{-2} similar in form to eq.(1) differs in substance from it, since the terms in front of T and T^{-2} contain /582 the temperature-dependent quantities $C_p^{a\,t}$ and $C_v^{a\,t}$. To simplify eq.(3), let us represent the term $(C_p^{a\,t})^2$ in the form of the product $C_{p\,298}^{a\,t} \cdot C_v^{a\,t}$. To compensate the error resulting from this assumption, we must seek a new value for the coefficient of K in the second term, and determine the multiplier in front of T^{-2} from $C_{p\,298}^{a\,t}$, as the coefficient c in eq.(1):

$$C_p^{aT} = 5.96 + \frac{K \cdot C_{p298}^{aT} \cdot C_v^{aT}}{T_{mp}}\,T - cT^{-2}. \tag{4}$$

If, in eq.(4), we substitute the expression (Bibl.6) for $C_v^{a\,t}$

$$C_v^{aT} = 6.6 - 0.87 \cdot \frac{\Theta}{T} ,$$

we obtain

$$C_p^{aT} = \left(5.96 - \frac{a_0 \cdot C_{p298}^{aT} \cdot \Theta}{T_{mp}}\right) + \frac{b_0 \cdot C_{p298}^{aT}}{T_{mp}}\,T - cT^{-2} ,$$

las (6), (7), and (8). With this object, from eqs.(1) set up according to eqs.(6), (7), and (8), we calculated the heat capacities at 400, 600, and 800° K, and so on, and compared them with the experimental data (Bibl.1). In this case, we calculated in percent the relative deviation δ of the calculated value of C_p

TABLE 1

DEVIATIONS BETWEEN CALCULATED AND EXPERIMENTAL VALUES OF THE
HIGH-TEMPERATURE HEAT CAPACITY FOR A NUMBER OF SOLID
INORGANIC COMPOUNDS

Substance	δ, % max	$\bar{\delta}$, %	Interval °K	Substance	δ, % max	$\bar{\delta}$ %	Interval °K
Li$_2$O	−11.6	−5.7	298 − 1000	MnS	+ 2.7	+ 1.6	298 − 1800
BeO	− 9.9	±3.9	238 − 1200	B$_4$C	− 8.5	± 4.5	298 − 2000
MgO	+ 3.9	±2.0	298 − 2000	TiC	− 3.7	− 3 0	298 − 2000
CaO	− 1.6	−1.1	298 − 2000	Cr$_7$C$_3$	−13.0	− 7.8	298 − 1400
SrO	− 4.1	−3.3	298 − 1800	VN	− 8.2	− 4.2	298 − 2000
BaO	− 3.4	− 2.5	298 − 2000	ZrN	− 7.1	− 3.4	298 − 2000
ZnO	− 2.0	±1.0	298 − 2000	LiAlO$_2$	− 1.2	− 0.8	298 − 1800
MnO	− 1.3	+0.5	298 − 2000	MgAl$_2$O$_4$	− 6.1	± 2.5	298 − 2000
V$_2$O$_4$	− 8.9	−6 2	298 − 2000	CuAl$_2$O$_4$	+ 4.4	+ 3.1	298 − 1800
La$_2$O$_3$	− 1.2	±0.5	298 − 2000	Na$_2$SiO$_3$	− 5.5	− 2.7	298 − 1200
TiO$_2$	+12.2	±4 8	298 − 2000	Mg$_2$SiO$_4$	− 2.9	± 1.6	298 − 2000
HfO$_2$	− 5.9	±3.8	298 − 2000	CaSiO$_3$	+ 3.8	+ 2.8	298 − 1400
ThO$_2$	− 6.5	±2.6	298 − 2000	CaFe$_2$O$_4$	+ 7.3	+ 3.4	298 − 1400
Nb$_2$O$_5$	+ 7 0	+ 4.9	298 − 1600	FeCr$_2$O$_4$	− 2.5	− 1.0	298 − 1800
Ta$_2$O$_5$	+ 2.3	±1.1	298 − 2000	Fe$_2$SiO$_4$	− 2.6	± 0.9	298 − 1400
MoO$_3$	+ 2.4	+1.9	298 − 1000	Na$_2$CO$_3$	− 6.4	± 2.6	298 − 1000
LiF	− 7.1	−4 1	298 − 1000	Ba (NO$_3$)$_2$	+ 8.1	+ 4.4	298 − 800
NaF	− 4.8	−2.1	298 − 1200	Al$_2$(SO$_4$)$_3$	+ 5.4	+ 3.0	298 − 1000
NaCl	− 0.3	−0.1	298 − 1000	MgTiO$_3$	− 4.3	− 2.6	298 − 2000
KF	+ 3.1	±1.1	298 − 1000	BaTiO$_3$	+ 8.5	+ 3 7	298 − 1800
KCl	+ 2.3	±1.2	298 − 1000	Ba$_2$TiO$_4$	±10.5	± 4.6	298 − 1800
AgCl	− 4.6	−2.4	298 − 700	Al$_2$TiO$_5$	+ 0.9	+ 0.6	298 − 1800
CaCl$_2$	+ 9.9	+4.8	298 − 1000	FeTiO$_3$	+ 1.6	± 0.7	298 − 1600
MnCl$_2$	+ 7.0	+3.1	298 − 900	CaTiSiO$_5$	+ 6.3	+ 3.9	298 − 1600
FeCl$_2$	+ 8.3	±3.5	298 − 900	CaB$_2$O$_7$	+ 7.6	+ 4.2	298 − 1200
NiCl$_2$	+ 3.4	±1.2	298 − 1200	Ag$_2$Al	+ 0.6	+ 0.4	298 − 900
FeCl$_3$	− 3.8	−2.5	298 − 550	MgZn$_2$	+ 2.4	+ 1.8	298 − 800
UCl$_4$	+ 5.7	+3.5	298 − 700	MoSi$_2$	+ 1.7	± 0.8	298 − 1200

from the experimental value, as well as the mean deviation $\bar{\delta}$ for the temperature interval considered. The results of these calculations are given in Table 1, dealing with the principal types of inorganic compounds: oxides, halides, /584 carbides, nitrides, aluminates, silicates, etc. In selecting these compounds, we were mainly concerned with the fact that in some cases the experimental values of the high-temperature heat capacity may differ greatly from the true values if obtained by a differentiation of only moderately accurate enthalpy equations.

It will be seen from Table 1 that the proposed rapid method of calculating C_p gives entirely satisfactory results for most compounds ($\bar{\delta} < 5\%$) and that the mean deviation $\bar{\delta}$ for the 56 substances considered does not exceed $\pm 3.0\%$.

In cases where a polymorphic transformation of the substance[*] is observed in the interval $298 - T_{mp}$, the melting point in eqs.(6) and (7) must be replaced by the temperature of polymorphic transformation T_{tr} (Bibl.6), yielding an equation of the type of eq.(1) from the low-temperature α-modification of the substance in the interval $298 - T_{tr}$.

It is difficult to solve the problem of a computational determination of the heat capacity equation for the high-temperature β-modification of a sub-stance. In first approximation, however, eqs.(6) and (7) may be used to set up an equation of the type $C_p^{at} = a + bT$ for the β-form of a substance, by substi-tuting the value of C_{p298}^{at} by the value of the heat capacity at the transition point, calculated by the equation of the α-modification of the compound, and substituting Θ by the value of Θ_β characteristic for the β-form of the sub-stance. An approximate formula for calculating Θ_β is easily obtained by extend-

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[*] Substances with a ferromagnetic transformation are not considered in this paper.

5

ing the Lindemann hypothesis (Bibl.10) on the melting of a crystal during poly-
morphic transformation. In that case, for the α- and β-forms of the compound,
the well-known Lindemann formula (Bibl.10) is obtained for the characteristic
temperature, represented in the form of the equations

$$\Theta_\alpha = 133 \, (T_{tr} \cdot M^{-1} \cdot V_\alpha^{-2/3})^{1/2} , \qquad (9)$$

$$\Theta^\beta = 133 \, (T_{mp} \cdot M^{-1} \cdot V_\beta^{-2/3})^{1/2} , \qquad (10)$$

where M is the atomic mass, and V is the atomic volume of the compound. Com-
bining eqs.(9) and (10) under the assumption that $V_\alpha \approx V_\beta$, we obtain

$$\Theta^\beta = \Theta_\alpha \left(\frac{T_{mp}}{T_{tr}} \right)^{1/2} ,$$

where Θ_α is calculated from eq.(5).

Taking these corrections into account, we set up the equations of high-
temperature heat capacity for substances with a polymorphic transformation in
the interval 298 – T_{mp} . The calculated values of C_p were compared with the
experimental values (Bibl.1). The results of the calculations for 12 compounds
are given in Table 2, according to which the mean deviation $\overline{\delta}$ for the α-modifi-
cation of these substances is ±3.5% and for the β-modification, ±8.0%. It /585
is obvious that the proposed method of calculating C_p is characterized by a
relatively low accuracy for the β-form of the compound. This is due to the
approximate character, both of the proposed computational formulas and of
certain experimental data used in the comparison.

In the absence of an experimental value of S_{298}^{at} for the test substance, in
calculating C_p by this method, we may use its approximate value determined by
the empirical methods of the literature (Bibl.2. 11, 12). It has been estab-
lished, by the aid of special calculations, that any fluctuation of the values
of S_{298}^{at} and T_{mp} within a range of ±10% leads to an average decrease of ±0.5

6

to 1.0% in the accuracy of the equations obtained for C_p. If the calculated value of C^{at}_{p298} is used, it should be qualified by an error of < 5%. The

TABLE 2

DEVIATIONS BETWEEN CALCULATED AND EXPERIMENTAL VALUES
OF THE HIGH-TEMPERATURE HEAT CAPACITY FOR CERTAIN SOLID
SUBSTANCES WITH A POLYMORPHIC TRANSFORMATION IN THE
INTERVAL 298 - T_{mp}

Substance	δ, % max.	$\bar{\delta}$, %	Interval °K	Substance	δ, % max.	$\bar{\delta}$, %	Interval °K
α—TiO	− 9.2	− 5.3	298—1264	β− $Ca_3(PO_4)_2$	−14.1	± 6.0	298−1373
β—TiO	−16.8	−16.2	1264—2000	β− $Ca_3(PO_4)_2$	+12.2	+ 9.9	1373−1600
α—Quartz	+ 6.3	+ 3.6	298—848	α—Na_2TiO_3	− 4.4	− 2.2	298−560
β—Quartz	+14.2	+ 9.7	848−1800	β—Na_2TiO_3	−14.6	− 9.4	560−1300
α−AlF_3	− 1.5	± 0.5	298—727	Na_2SO_4·III	− 5.0	± 1.6	298−514
β−AlF_3	+ 6.8	+ 3.3	727—1400	Na_2SO_4·I	− 7.8	− 3.9	514−1100
α—SnS	+ 3.0	± 1.7	298—875	α−K_2SO_4	− 4.6	± 1.8	298−856
β—SnS	+12.7	+12.5	875−1150	β−K_2SO_4	+ 2.2	+ 1.4	856—1300
α—CaC_2	+11.1	+ 6.1	298−720	α−$Ca_2P_2O_7$	+ 4.5	+ 2.6	298−1413
β—CaC_2	+10.5	+ 8.7	720—2000	β−$Ca_2P_2O_7$	+ 6.2	+ 4.3	1413−1600
α—$CaTiO_3$	+ 7.9	± 3.1	298−1530	α—Mn_3C	−10.3	− 7.7	298−1310
β—$CaTiO_3$	+15.8	+11.4	1530—2000	β−Mn_3C	−24.9	−23.5	1310—1500

additive-entropy method developed by one of us (Bibl.13) must be considered as most suitable for the approximate calculation of C^{at}_{p298}. This method is accurate within ±5.0% and may be successfully used with this method of setting up the equations of the high-temperature heat capacity of solid inorganic compounds.

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